Parallel Beam Powder Diffractometry Using a Laboratory X-Ray Source

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Abstract

We report on the application of a new, non-dispersive double multilayer optical arrangement to prepare a parallel beam from a laboratory x-ray source for standardization of powder diffraction reference materials and the associated high accuracy diffractometer. The beam preparation optic uses a graded-spacing parabolic multilayer to gather radiation from a small focus x-ray source and a subsequent planar multilayer with spacing near the mean of the graded multilayer to redirect the radiation toward the powder specimen. Diffracted radiation, after analysis by a well-characterized Soller collimator, is registered in a proportional counter. The instrumental geometry permits wide range symmetrical scanning about the incident beam direction allowing elimination of errors associated with zero diffraction angle location. Initial performance metrics of the present diffractometer and the availability of accurate, optically-based profile parameters for the Cu Kα doublet connected to the base unit for length by x-ray (lattice) interferometry, assure that future standard reference powder samples will be certifiable to within parts per million.

Background and motivation

The vast majority of powder diffraction measurements use conventional laboratory x-ray sources (including rotating anodes) with parafocussing optics to accommodate the low signal levels intrinsic to powder samples. Unfortunately, achieving this gain in signal level entails concomitant sensitivities to sample positioning and beam penetration depth which exclude such measurements from first-principles accuracy. Instead, such measurements often rely on externally supplied powder diffraction standards used either sequentially or, more frequently, mixed with the subject specimen to provide 'internal' standardization.

NIST, as the primary provider of the needed standard reference materials (SRM's), currently faces a diminishing inventory whose accuracies are limited by the methods used in their certification [1]. In this circumstance, we have undertaken to devise a robust procedure for first-principles standardization of the next generation of powder SRM's with improved connection to the base unit for distance in the international system of units, the SI. It is particularly useful to take advantage of the progress made in the last 20 years in connecting the lattice spacings of certain highly perfect single crystals with optical realizations of length in the SI.

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Among the requirements for a first-principles (standards-free) measurement are the use of parallel beam optics, and registration of geometrically complementary patterns, *i.e.*, scans taken both clockwise and counter-clockwise with respect to the incident beam direction, as well as accurate measurement of the angular displacements. The use of parallel beam geometry eliminates all sensitivity to the sample's centration, and the penetration depth of the radiation. Similarly, symmetric scanning removes the need to invoke an auxiliary operation to locate the diffractometer's zero point. The procedures we describe are straightforward and can be applied in other laboratories to reproduce our results or wherever standards-free measurements are needed. They are, however, designed for highly accurate studies of relatively simple patterns and are not well suited to rapid analysis or complex patterns.

The advantages of parallel beam diffractometry are well known and have motivated the establishment of beamlines dedicated to powder diffraction measurements at synchrotron radiation facilities [2]. The instrumental configurations of these beamlines have been chosen to realize many of the advantages of parallel beam optics without, however, addressing the need to map mirror-symmetric reflections, or providing means to accurately establish the incident wavelength; both steps are required for first principles measurements.

Beam preparation optics

We examined a wide range of beam preparation optics, beginning with a strong inclination to the use of highly perfect monocrystals in quasi-non-dispersive arrangements. While these crystal-based options have many advantages, including ease of realization with silicon and germanium, the high spectral resolution inherent in crystal diffraction optics entails a potential imprecision in tuning to the peak of, let us say, $K\alpha_1$. In addition, while perfect crystal optics are very successfully used in beam preparation for powder diffraction with synchrotron radiation, when they are used with a laboratory source, data rates become very low.

Large gains in flux have been realized in recent times by use of graded-spacing multilayers on parabolic substrates [3]. The use of such elements to feed crystal diffractors or monochromators (including Bartels configurations) has been discussed extensively [4]. Although we gave extended consideration to this approach, certain practical limitations recommended against it in our application. The first problem is that it shares, to some extent, the same difficulties as noted above for the case of a perfect crystal beam conditioner. The flux deficit is clearly reduced but nevertheless remains significant. The wavelength indeterminacy requires routine re-mapping of the profile to assure stability of the delivered wavelength.

In the end we have developed a new approach to beam preparation for powder diffraction by combining a graded-spacing parabolic diffractor with a flat multilayer optic having a grating spacing equal to the mean value of the spacing of the graded multilayer [5]. We arrange these in a non-dispersive configuration as suggested in the diagram shown in Fig.

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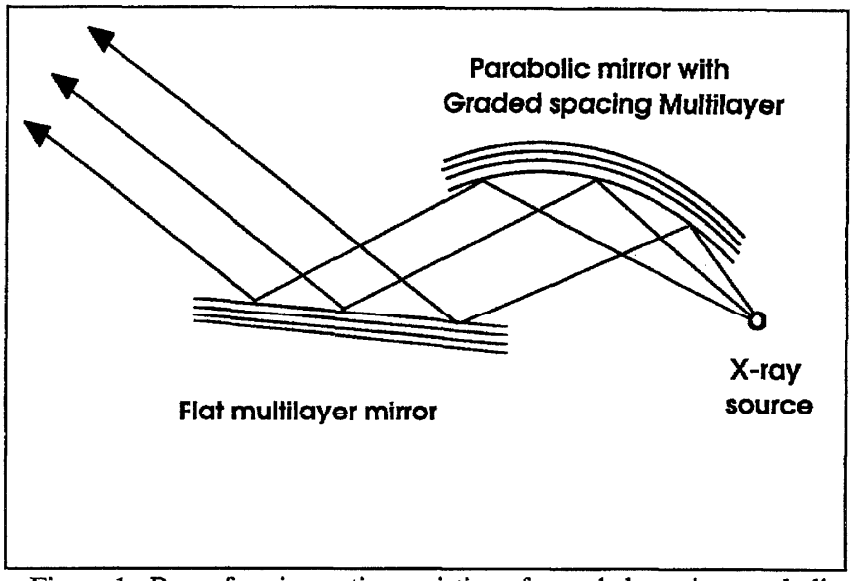

Figure 1. Beam forming optic consisting of a graded-spacing parabolic multilayer followed by a planar multilayer with a d-spacing equal to the mean value of the collimating reflector.

a value which results in very small wavelength dispersion from either multilayer, while the "minus" configuration effectively allows the two dispersions to nearly cancel. The effect of these choices is to provide a beam filtered by the diffractors but still including, with no perceptible distortion, both components of the Kα doublet; the effective passband is approximately 50 eV, which should be compared with the 20 eV separation of the doublet components and the much narrower linewidths of the individual components. The beam is nonetheless well collimated with an angular spread of approximately 0.01°. The small spectral dispersion should allow use of optically based, high accuracy doublet profiles, as will be discussed below, thereby eliminating wavelength setting imprecision. In addition, flux levels delivered to the powder sample, as shown below, are high enough for convenient measurement cycle times with a modest (2 kW) laboratory x-ray source. Finally, the very small dispersion means that profiles on both sides of zero angle have closely similar appearance for sufficiently large diffraction angles; they differ because the intrinsic powder dispersion is on one side proportional to ($\tan\theta$ + tan 1°) while on the other side it is proportional to ($\tan\theta$ – tan 1°). Use of other anode materials requires retuning of the multilayer elements or interchange of other pre-aligned pairs.

Diffractometer design

The general disposition of our new diffractometer is indicated in Fig. 2 where we show the geometry for diffraction on both sides of the zero angle at 2θ =±90°; the single

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Bragg angle (θ) of 45°; these are separated by 4θ. The input beam preparation optic is as described above. The exit Soller collimator and proportional counter detector are carried by a large (80 cm dia.) rotary platform driven by a stepping motor through relatively imprecise spur gearing. The platform's rotation is, however, monitored by a high resolution optical incremental encoder with 12000 cycles per revolution and a 2-station readout whose calibration and performance are described below. The powder sample is mounted on a separate, worm-driven rotary stage which surmounts the

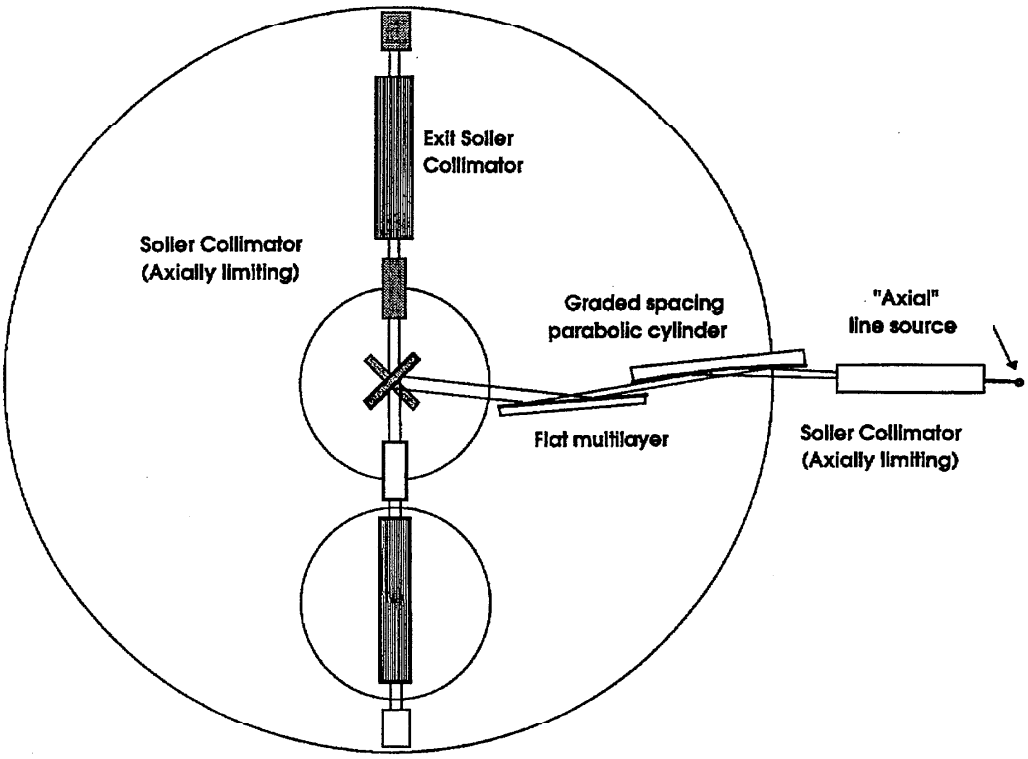

Figure 2. Functional layout of parallel beam powder diffractometer (neither components nor distances are to scale). The sample, exit Soller collimator, and detector are shown in positions corresponding to a Bragg angle of 45°.

main platform. By driving the sample stage at half the platform speed in the opposing direction, we maintain the conventional $\theta - 2\theta$ configuration. Sample rotation about the diffraction vector is effected by a spinner motor whose drive passes through the encoder and both rotary stages; particle statistics can be further improved by rocking the sample through a few degrees during data accumulation. When using the reflection geometry shown, the scan must be interrupted at zero degrees to allow the sample to be rotated by 180° (so as to present the same sample surface to the beam) before proceeding into the other diffraction sector.

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While the present report is not intended to provide a detailed description of the instrumentation and procedures, a few technical comments are in order. The overall system is under computer control and uses encoder-guided, software-implemented rotation control to overcome its mechanical limitations. Although the angle encoder in use at the present time had an established calibration history, we believe that routine *in situ* calibration of the angle scale is needed if one wants to obtain defensibly accurate measurement of diffraction angles; our procedure is based on the use of an interferometrically calibrated optical polygon to get a correction table for large angular displacements, and application of a rotating optical wedge to map local interpolation errors [6]. We expect the final angular calibration to provide for robust estimates of the measured (4θ) intervals at the 0.5 sec level, thereby contributing insignificantly to the final error budget for Bragg angles around 40° and above.

The high degree of beam collimation provided by the input multilayer doublet means that, aside from intrinsic broadening and axial divergence (limited to ±0.75° by the axial collimator shown), the dominant resolution limiter is the exit Soller collimator. In our experience to date, this is a very significant problem, particularly since our goal is total profile fitting. To convey a sense of the problem, Fig. 3 shows angular transmission profiles for two of the collimators we have studied that indicate the currently significant limitation arising from this component. From the indicated transmission function measurements, it is clear that the higher resolution collimator has an unpleasantly complex transmission profile including high and asymmetric off-axis transparency; the indicated asymmetry reverses as expected when the collimator's input and output directions are interchanged. Our most effective collimator is, in fact, the one having poorer angular resolution but, as can be seen in the upper part of Fig. 3 a rather symmetric profile with low transmission in the 'tail' region. While the contribution of total reflection to this profile is suggested by the shape, this level of detail has not been further explored in anticipation of planned technical improvements.

We have chosen to use a xenon proportional counter for x-ray detection for several reasons: The first is to reduce sensitivity to higher order x-radiation and gain improved energy discrimination for background reduction. The second reason is simply mechanical in that our experimental configuration is intolerant of the additional extension along the diffracted beam direction required by a conventionally configured scintillation counter with its attached end-window photomultiplier.

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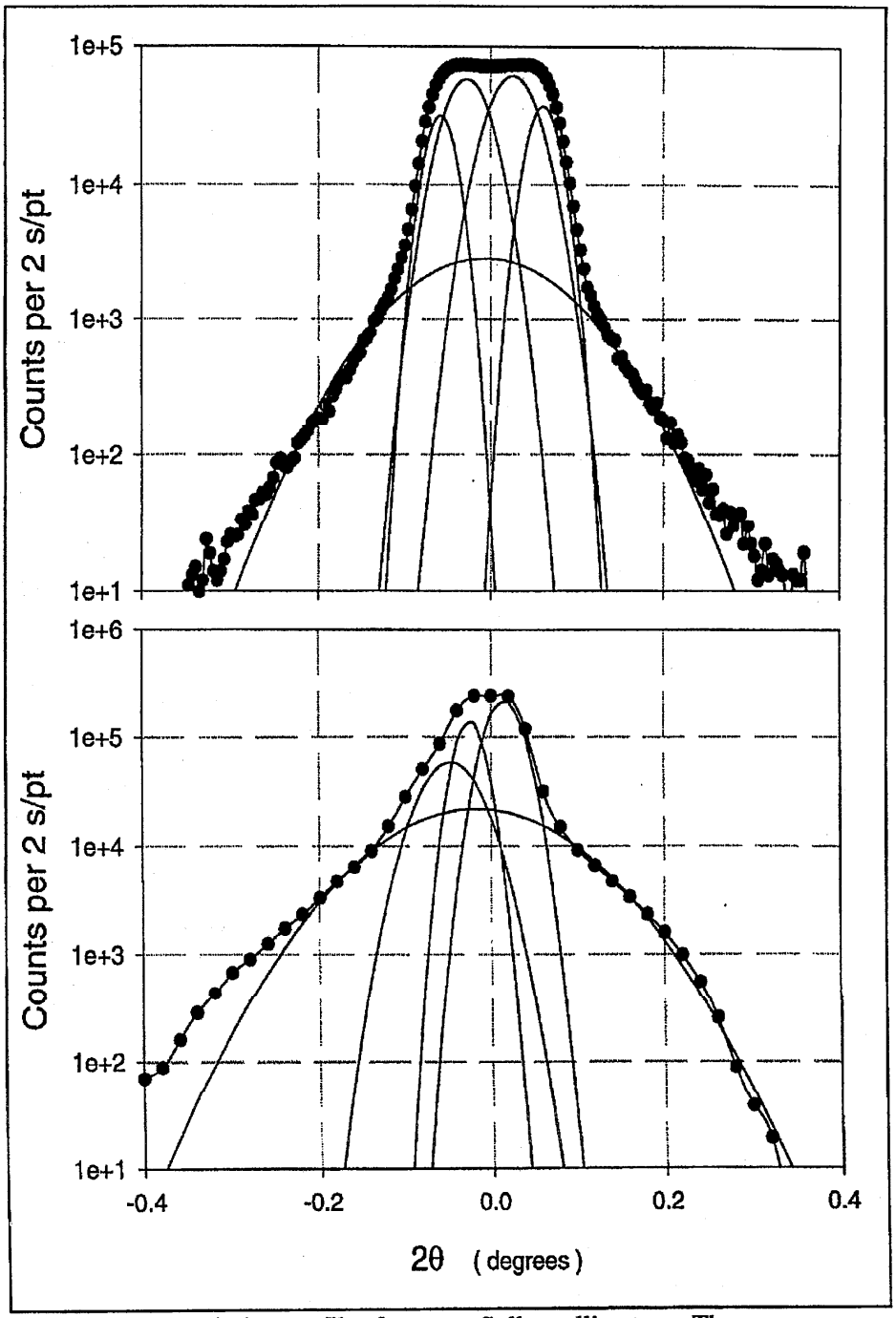

Figure 3. Transmission profiles from two Soller collimators. The upper curve is from a (formerly) commercial product with a resolution of 0.12°. The lower panel came from a prototype collimator having 0.08° resolution but with large and asymmetric transmission in the tail regions.

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Performance metrics

We first present in Fig. 4 diffractometer profiles obtained in three regions of 2θ from a silicon powder sample initially considered as a replacement for SRM640b. All data were obtained with the source operating at 40 kV and 50 mA. At low angles, the Kα doublet is unresolved while near 2θ = 90°, and surely above 2θ = 90°, the doublet's principal components are clearly resolved. The broad spectral acceptance of the beam preparation optic includes the entire doublet, allowing use of a recently available, highly accurate determination of the Cu Kα spectral profile [7]. This high resolution, single- and double-crystal spectrometer study used a silicon monocrystal whose grating spacing had been established relative to that of the silicon material used in a well-documented optical determination of the its lattice period [8]. Reference 7 provides model functions and the associated parameters needed to describe the entire Cu Kα doublet on a wavelength scale with an estimated standard uncertainty of approximately 10^{-6}Å (0.1 fm), well beyond the known requirements of powder diffraction standardization.

To test for the absence of spectral distortion due to the beam preparation optic, we chose as a model function a parametrized Voight expression with separate Lorentzian and Gaussian width parameters. The Lorentzian width was taken from the emission profiles of Ref. 7 while the Gaussian width was a free parameter representing the composite contributions of the various optical elements. The axial collimation is sufficiently restricted that for all reflection profiles, with the possible exception of (111), no influence of the powder diffraction ring curvature can be detected. The residues from the fitted data in Fig. 4 show no systematic pattern indicating that the incident doublet is indeed transmitted by the preparation optic without significant distortion. This is an important result in that it means that the recorded patterns are, in effect, internally standardized. This issue will require continued examination with greater statistical precision and with higher resolution exit collimation, but for the moment, the situation is reassuring.

Figure 5 shows the profile from an alumina sample (SRM1976) in the neighborhood of a closely spaced pair of reflections involving the (0,1,10) and (2,-1,9) planes. The figure shows the components of the fitted profile and the residuals from this model. It should be noted that the parameters used in these fits, except for some additional instrumental broadening, are those obtained from the high resolution, high accuracy studies reported in reference [7] and are not adjusted in the fitting process. Our preliminary data analyses were carried out with a commercial profile fitting package not specifically adapted to powder diffraction profiles. The fitting program provides estimated standard errors for the parameters emerging from the least squares procedures which, for 2θ near 90°, is approximately 0.0005°. The effect of combining two such locations to obtain a value for an interplanar spacing results in a relative uncertainty estimate near 1×10^{-6}. If one makes use of the redundancy inherent in powder diffraction, and the symmetry properties of the unit cell, it is not unreasonable to expect that the standardized materials may approach a level of estimated relative standard uncertainty near 10^{-6}.

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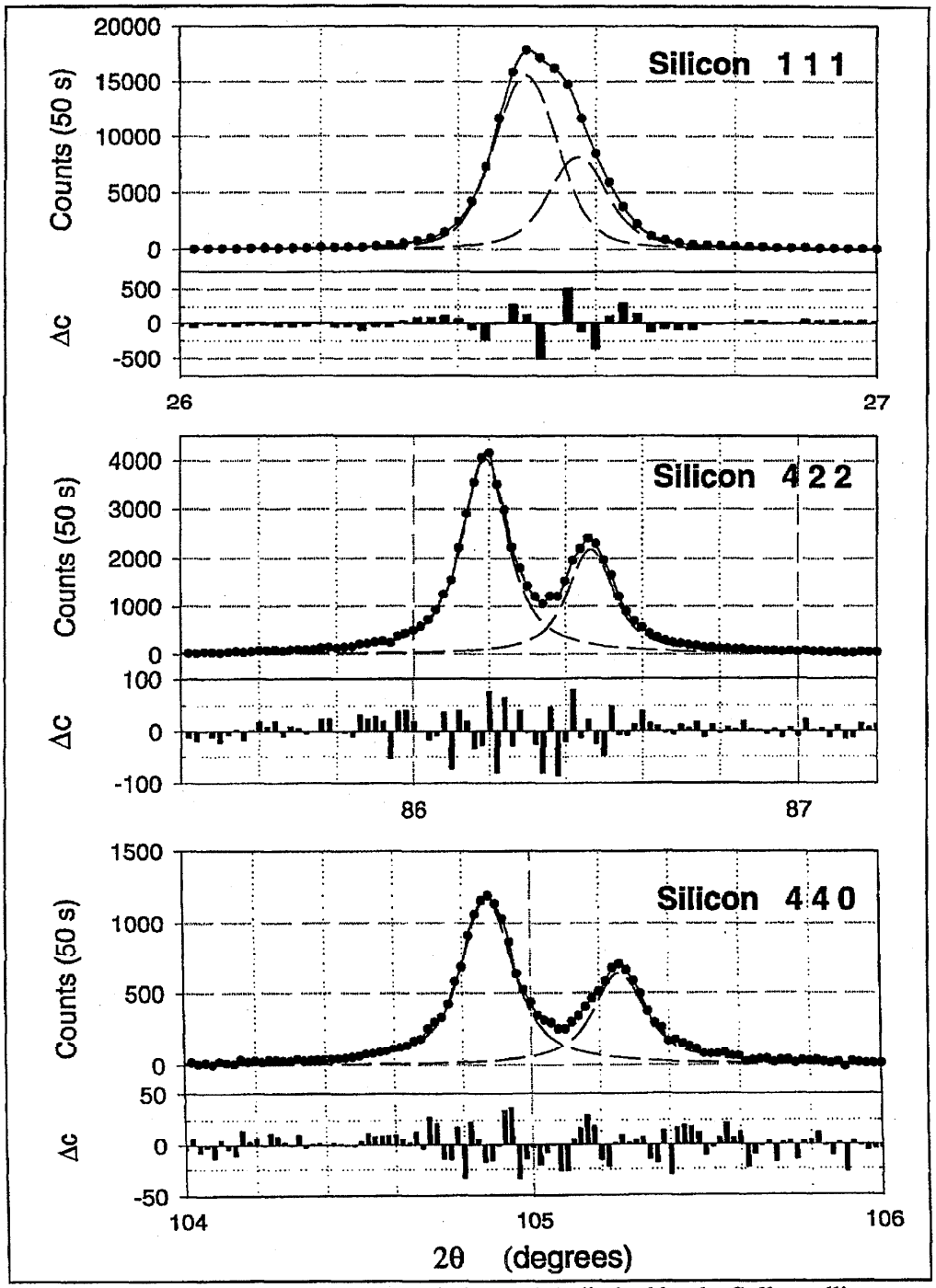

Figure 4. Powder profiles indicating resolution mainly limited by the Soller collimator. The angular scale is only approximate since these scans were taken before encoder calibration and without the use of symmetric scans as required to avoid zero offset error in the 2θ scale. Dashed profiles are the fitted peaks (see text), and the dashed horizontal line is the baseline (background level).

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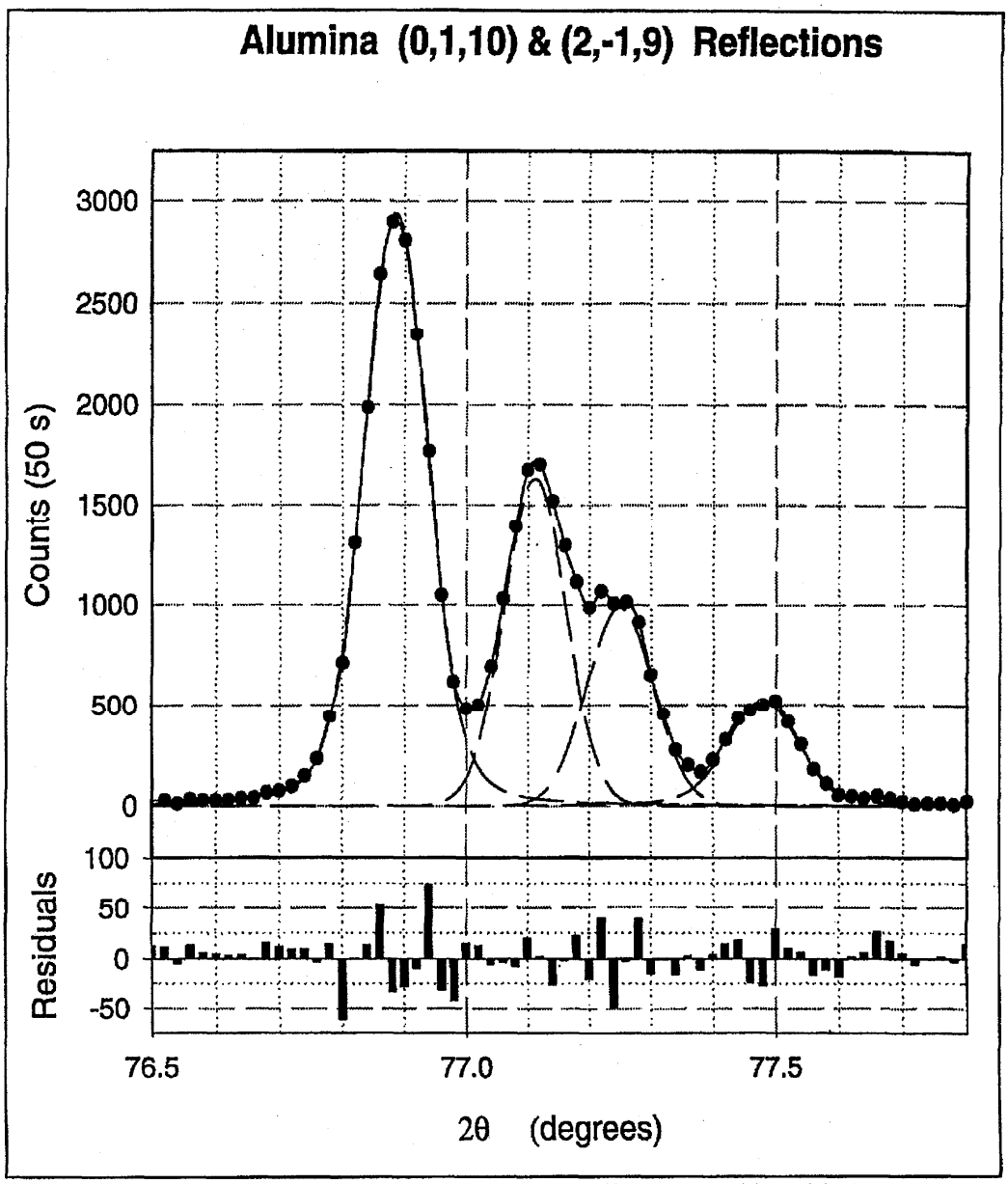

Figure 5. Powder scan through the (0,1,10)-(2,-1,9) diffraction doublet with the associated residue distribution. See remarks in the caption of Fig. 4 concerning the angle scale and the meaning of the dashed lines.

The level of precision identified above required the long counting times shown in the figures and would lead to some tens of hours for a full scan of the detector on both sides of zero. In the applications for which our apparatus and procedures are designed, such complete scans are not contemplated. For the most part, limited scan regions around several reflections with Bragg angles between 30° and 60° will be identified and a

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measurement protocol established concentrating observation time on acquiring data covering regions of a few degrees around each.

Outlook for a new family of powder SRM's

The need for a new inventory of powder standard reference materials (SRM's) has been evident both to the user community and to NIST. Meeting this need requires not only the kind of metrology development described in this report but also extensive investigations of materials sources and highly refined preparation protocols. For example, we have already determined that the new inventory of a silicon line position standard will have to come from rather pure (i.e., undoped) high quality single crystal material, carefully screened for gradients in lattice parameter particularly along the growth direction. Of course, we must provide for extraction of a restricted range of particle sizes from the crushed and jet-milled single crystals. Finally, we are trying to identify a suitable passivation procedure to reduce long-term lattice changes due to oxide growth.

Where we stand in this process at the present time is suggested by the lattice metrology discussed in the present report and the brief comment on the materials problems given above. While there are several problems yet to be solved, we believe that a new set of protocols has been identified and that their technical feasibility has largely been demonstrated. The next year seems to be one of consolidation and the start of a production cycle. Our intent is that a powder SRM inventory for the next decade will emerge and that procedures for its subsequent renewal will have been established.

Conclusions

We have demonstrated the use of a novel, non-dispersive double multilayer optic and a high accuracy broad range diffractometer for standardization of powder diffraction reference materials. The beam preparation optic produces an x-ray probe beam with low angular divergence and high flux. The pass band of the optic is sufficiently broad that the entire Cu Kα doublet is passed without significant distortion, thereby providing unambiguous calibration. Several aspects of the diffractometry described in this report would appear to have potential applications outside the standardization application for which it was developed. For example, investigators might encounter a problem in which the small additional uncertainty arising from the use of an internal or substitutional standard is limiting. In this case, the 'standards-free' procedure we describe may be appropriate for direct application since it is readily duplicated with modest resources. Also in cases where penetration effects are large and/or surface location uncertain or ill-defined, parallel beam powder diffraction may be the modality of choice. The beam preparation optics described here offer a convenient means for approaching such problems requiring only modest diffraction apparatus and a conventional laboratory x-ray source.

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